

**RING-OPENED AZLACTONE INITIATORS FOR NITROXIDE-MEDIATED  
POLYMERIZATION**

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*US 6,680,362 B1*  
This application is a divisional of U.S.S.N. 10/358767, filed February 5, 2003, now allowed, the disclosure of which is herein incorporated by reference.

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Field of the Invention

The present invention provides initiators for nitroxide-mediated radical polymerization (NMP) processes.

Background

15 In conventional radical polymerization processes, the polymerization terminates when reactive intermediates are destroyed or rendered inactive; radical generation is essentially irreversible. It is often difficult to control the molecular weight and the polydispersity (molecular weight distribution) of polymers produced by conventional radical polymerization, in order to achieve a highly uniform and well-defined product. It is  
20 also often difficult to control radical polymerization processes with the degree of certainty necessary in specialized applications, such as in the preparation of end functional polymers, block copolymers, star (co)polymers, and other novel topologies.

In a controlled radical polymerization process radicals are generated reversibly, and irreversible chain transfer and chain termination are absent. There are four major  
25 controlled radical polymerization methodologies: atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), nitroxide-mediated polymerization (NMP) and iniferters, each method having advantages and disadvantages.

Nitroxide mediated radical polymerization (NMP) has been described as a simple, versatile and efficient controlled radical polymerization process. See, e.g., C.J. Hawker et al., "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations",  
30 *Chemical Reviews*, 2001, pp. 3661-3688. NMP processes employ an alkoxy amine as an initiator to produce a polymeric radical in the presence of a monomer.